Activated Carbon Based Adsorptive Natural Gas Storage

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Abstract

Natural gas is one of the major clean fuels that receive attention as it possesses cost competitive and lower emission features compared to gasoline. Liquefied natural gas (LNG) and compressed natural gas (CNG) have been applied in natural gas vehicles, while adsorbed natural gas (ANG) and natural gas hydrate (NGH) are still being studied in order to reduce the capital and operating costs. The main challenge that confronts ANG vehicle is the extension of driving range. Studies on gas storage capacity, delivery of natural gas and future research directions of activated carbon based adsorbents, aiming to achieve the stored volumetric efficiency correspond to the current CNG system, have been reviewed.

Keywords: Natural gas; Storage; Activated carbon; Adsorbents.

1. Introduction

The interest in natural gas as a vehicular fuel has grown promisingly since the beginning of the 1980s [1]. Natural gas has become an attractive fuel as it has considerable advantages over conventional fuels. With air quality issues gaining prominence around the world, natural gas has become one of the most promising alternative fuels because of its inherent clean burning characteristics [2, 3]. Natural gas vehicles (NGVs) have the potential to lower polluting emissions, especially in urban areas. Among the environmental benefits of using natural gas is lower in ozone levels as it has lower hydrocarbon emissions [1, 4]. The harmful tailpipe emission is reduced significantly as compared to gasoline vehicles with 99% less CO, 30% less NO*x* and 96% less HCs in emission [5].

In addition, natural gas offers lower fuel price as comparison to gasoline and diesel fuels [1, 2, 4]. From economic point of view, natural gas is very competitive as the commodity and distribution costs for natural gas are lower than those of gasoline and diesel. The NGV refueling station can be installed at almost any location where natural gas distribution pipeline is available. However, NGV is currently at a disadvantage since it is relatively high cost in production since gasoline and diesel vehicles benefit from decades of optimization and high volume manufacturing. Most of the NGVs on the road are simply gasoline vehicles converted to operate on natural gas. As a result, the fuel storage system and engine performance are not optimized for natural gas [4]. Despite this, NGV can still compete with conventional vehicles because of the lower fuel cost and less maintenance [1, 5]. As reported by Vasiliev *et al.* [5], the time of car application of NGV is extended up to 1.5 as compared to liquid fuel car, while the time of the oil service is increased up to 1.5 – 2. The noise of the working engine can be reduced down to 7 – 9 dB with the period of ignition system service is extended up to 40%.

2. Natural Gas Storage

Natural gas consists of about 95% methane with the exact composition varies between different parts of the countries and different refineries [6]. Due to its supercritical characteristic in standard temperature and pressure, natural gas has a very low density. The main disadvantage of natural gas is the low volumetric energy density compared to conventional liquid fuels [2, 3, 7, 8]. In order to overcome this problem, few storage systems, compressed natural gas, liquefied natural gas, adsorbed natural gas and natural gas hydrate, have been introduced with the continuous effort to improve the onboard storage.

2.1 Compressed Natural Gas (CNG)

The most popular type of storage method is compressed natural gas (CNG) at high pressure (20 MPa) [8]. At ambient temperature (25°C), CNG has an energy density of less than 10 MJ per liter, which is much lower than that of diesel and gasoline with approximately 37 and 32 MJ per liter respectively. In such conditions, CNG is compressed to about 230 unit volumes to one unit volume of storage container. For the same driving range, CNG requires a storage tank with 3 times the volume of a gasoline tank. This has created challenges as there has only limited onboard spaces available [4]. Therefore, the compact onboard storage requires the use of expensive and heavy, high-pressure compression technology [6].

2.2 Liquefied Natural Gas (LNG)

Liquefied natural gas (LNG) is usually stored at -161°C as boiling liquid in cryogenic tank at approximately 0.1 MPa. LNG has higher volumetric energy density as compared to CNG with 23 MJ/l [1, 4]. However, studies on the use of LNG system generally are for fuel usage on long-haul vehicles such as trains, buses and trucks. This application requires specialized container design and refueling procedures as cryogenic temperature is involved [1, 9]. In addition, operational problem occurs if the vehicle is not operated frequently. The liquid gas slowly vaporizes and pressurizes the storage vessel which must be vented to the atmosphere if the vehicle does not use off enough fuel [4].

2.3 Adsorbed Natural Gas (ANG)

Adsorbed natural gas (ANG) on suitable microporous material offers an opportunity to NGV's further development. ANG technology is actively studied to overcome the problems faced by CNG storage system [3]. The use of adsorbent, such as activated carbon, zeolites and porous polymers, in storage vessels has lowered the storage pressure range from 3.5 to 4.0 MPa [4]. Among the available adsorbents, activated carbon exhibits the largest adsorptive capacity [7]. The volumetric storage density of ANG tested by Brookhaven National Laboratory can achieve 3/4 of CNG at 1/6 of the gas pressure [9].

2.4 Natural Gas Hydrate (NGH)

Natural gas hydrate (NGH) has drawn much attention as a new alternative for natural gas storage and natural gas safe transportation. In America, Japan and Norway, NGH as vehicle fuel has been studied and is considered as a feasible fuel. Gas hydrate has high storage capacity with approximately 170 m^3 methane gas in 1 m^3 methane hydrate [10]. However, gas hydrate is only stable under certain conditions ($T < 20°C$, $P > 2$ MPa). Therefore, the extraction and utilization of natural gas from hydrate is a challenge as the stored gas cannot be released by just reducing the pressure [11, 12]. The NGH technology is still under developed since its operational conditions and process are not well established [12, 13].

3. Adsorbed Natural Gas (ANG)

3.1 Early Stages of Development

During early stages of ANG development, suitable microporous materials are studied, in order to obtain the most attractive adsorbent for natural gas storage. Among the adsorbents tested, such as zeolites, porous silica, porous polymer, porous ceramic, organic gels and activated carbon, active carbon appears to be the most suitable adsorbents, presenting the highest ANG energy densities, and thus the highest storage capacities [1, 6, 7, 8, 14]. Although zeolites have shown relatively high packing densities, they have lower micropore volumes as compared to activated carbons. Besides, hydrophilic characteristic of zeolites has created methane adsorption capacity lost with time due to preferential moisture adsorption. In addition, the thermal conductivity of carbons is much higher than that of porous ceramics, thus gives advantage to the filling and delivering of natural gas which involve exothermal and endothermal processes respectively [1, 14].

The main issue of ANG storage is the stored volumetric efficiency as compared to CNG and conventional fuels [1, 7, 15]. In order to achieve the maximum volume of gas per volume of storage vessel (V/V), numerous studies have been carried out with different precursor materials and activation techniques to obtain high adsorption capacity activated carbon [1, 7, 8]. From these studies, it shows that ANG can provide adequate energy density at a low pressure (3.5 MPa) and room temperature [3, 9]. According to Wegrzyn and Gurevich [9] selecting either an ANG or a CNG system does not depend critically on storage efficiency as this value for both systems is similar, but the total system cost and performance.

However, ANG storage faces several problems which have hindered this technology from being widely commercialized. One of them is the management of the thermal effects that is related to the heat of adsorption. The heat of adsorption generated during charge has to be removed and resupplied during discharge in order to maintain the adsorption and delivery capacity [1, 6]. Besides, impurities in natural gas gradually contaminate the adsorbents with heavy hydrocarbons and water vapour, thus lower the storage capacity. In addition, capacity of the adsorbent decreases due to the residual amount of natural gas left at depletion [6, 16].

3.2 Recent Achievements

New technology of ANG has been actively studied in order to overcome problems faced during early stages. Continuous efforts have been done to increase the adsorption capacity by producing activated carbon with high microporosity. Recently, the methane adsorption capacity is enhanced by surface modification of activated carbon with metal oxides. Wang *et al.* [17] and Hattori *et al.* [18] reported that magnesium oxide and nickel oxide dispersion leads to enhancement of methane adsorptivity, which verified the study by Kaneko *et al.* [19].

On the other hand, the thermal effects of charging and discharging also receive great attention. The heat of adsorption released during charging will heat up the substrate and lower the methane adsorption capacity. During discharging, temperature drop of the bed will increase the amount of natural gas that remains in storage at depletion [6]. As a result, internal finned heater and heat pipe for thermal control have been suggested [5].

Study on wet activated carbon suggested a new alternative to store natural gas. It is claimed that all drawbacks of the traditional ANG were overcome in this new method. The heavier component of natural gas can form hydrate easily, and bed guard is no longer required. The thermal effect of fast charging and discharging is decreased to 1/10 of previous ANG. As a result, the storage capacity is not much affected. Furthermore, rapid discharge of complete methane shows that the charging and discharging process is reversible [12, 15, 16].

4. Future Research Directions

Development of adsorbents is the main criteria to improve the storage capacity of ANG. Research on surface modifications of activated carbon can be carried out using various metal oxides, such as aluminium oxide, calcium oxide, copper oxide, and zinc oxide. The relationship between the enhancement of methane adsorptivity and the manner of dispersion of different metal oxides is yet to be studied in detail. Different metal oxides will form various structures on the activated carbon which might be able to assist the physical adsorption of supercritical methane as metal oxides may preferentially interact and embedded in different supported states [17, 18]. Furthermore, concentration of the metal oxides dispersed should be studied as the deposition might either invade pore-opening effect or pore-blocking effects, which affect the adsorption capacity [17]. Besides, research on wet activated carbon on real application has to be carried out and improved as stated by Perrin *et al.* [15] that the hydrate formation kinetics are very slow and would affect the feasibility of practice. Furthermore, wet activated carbon study also arises another issue on selecting either the microporous or macroporous carbon material as adsorbent with crystallites are formed.

Proper storage design is essential for ANG to be commercialized. Development has to be done on shaped vessel designs which can be integrated with the vehicle shape to reduce the spatial intrusion within a vehicle [4]. Thermal control design in the tank is needed for better heat exchange to minimize the temperature fluctuations [4, 5]. Although ANG system operates at pressure much lower than CNG system, it must be designed as closely as possible to existing pressure vessel standard in the absence of specific codes. Careful manufacturing and design of the tank ensure the onboard safety of ANG vehicles [4].

5. Summary

ANG technology is an alternative to car manufacturers in developing higher performance NGVs which offer environmental benefits. High performance based on delivery has been achieved by carbon-based adsorbents. However, storage performance on limited space available onboard requires proper designation of the storage vessel. Non-cylindrical feature of ANG tank design allows better integration within vehicle structures. Collaboration of automobile manufacturers on this area would speed up the process to commercialize ANG technology. In addition, lower pressure (< 5 MPa) of ANG storage provides versatility in vessel design which is an advantage over CNG system.

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